Claims

Claims 1-93. **(cancelled)**

94. **(currently amended)** A kinetic resolution process, comprising the step of reacting a silyl azide and a mixture of stereoisomers of a chiral cyclic substrate in the presence of a non-racemic chiral catalyst to produce by kinetic resolution a stereoisomerically enriched cyclic substrate or a stereoisomerically enriched azide-substituted product or both, wherein said chiral cyclic substrate comprises a carbocycle or heterocycle having a reactive center susceptible to nucleophilic attack by said silyl azide, and said non-racemic chiral catalyst comprises an asymmetric tetradentate ligand complexed with a metal atom, which complex has a rectangular planar or rectangular pyramidal geometry.

95. **(previously presented)** The process of claim 94, wherein said silyl azide is a trialkylsilyl azide.

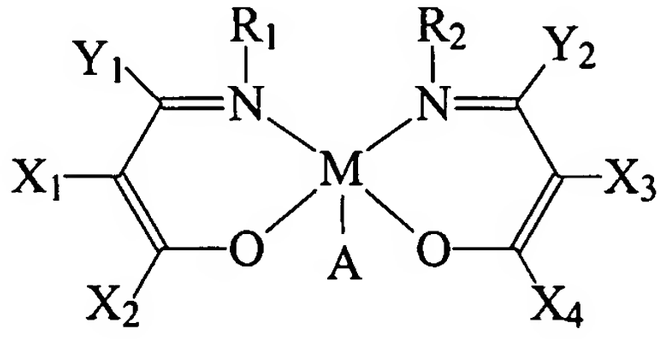
96. **(previously presented)** The process of claim 94, wherein said silyl azide is trimethylsilyl azide.

97. **(previously presented)** The process of claim 94, wherein the metal atom is a transition metal from Groups 3-12 or from the lanthanide series.

98. **(previously presented)** The process of claim 94, wherein the metal atom is selected from the group consisting of Co, Rh, and Ir.

99. **(previously presented)** The process of claim 94, wherein the metal atom is Co.

100. **(previously presented)** The process of claim 94, wherein the non-racemic chiral catalyst is selected from the group consisting of chiral crown ethers complexed with a transition metal atom; the chiral catalyst represented by **102**,



102

in which

the substituents R_1, R_2, Y_1, Y_2, X_1, X_2, X_3 and X_4 each, independently, represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro, thiol, amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or $-(CH_2)_m-R_7$,

or any two or more of the substituents taken together form a carbocycle or heterocycle having from 4 to 8 atoms in the ring structure, which ring structure may be a fused ring, as in the case of, for example, X_1 and X_2 forming a ring, or which ring may be a bridging ring, as in the case of R_1 and R_2, X_2 and X_4, or Y_1 and X_2 representing different ends of a single substituent,

with the proviso that at least one of R_1, Y_1, X_1 and X_2 is covalently bonded to at least one of R_2, Y_2, X_3 and X_4 to provide the β-iminocarbonyls as a tetradentate ligand;

R_7 represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle , or a polycycle;

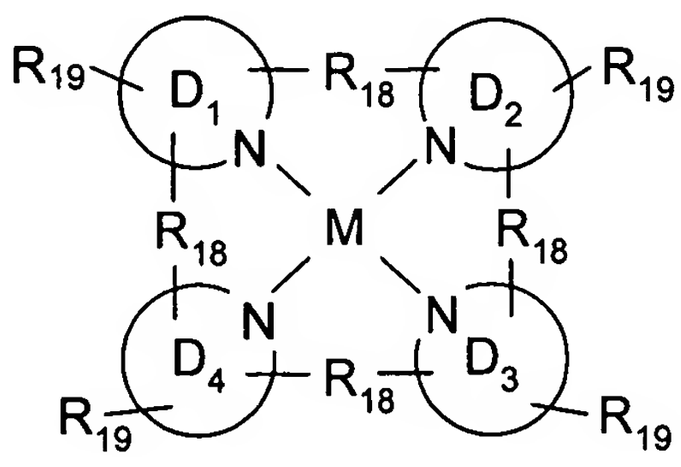
m is zero or an integer in the range of 1 to 8;

M represents a transition metal;

A represents a counterion or a nucleophile; and

the catalyst is asymmetric;

the chiral catalyst represented by **108**,



108

in which

D_1, D_2, D_3 and D_4 each represent heterocycles, such as pyrrole, pyrrolidine, pyridine, piperidine, imidazole, pyrazine, or the like;

each R_{18} occurring in the structure represents a bridging substituent which links adjacent heterocycles, and preferably contains at least one stereogenic center of the ligand. For example, each R_{18}, represents an alkyl, an alkenyl, an alkynyl, or $-R_{15}-R_{16}-R_{17}-$, wherein R_{15} and R_{17} each independently are absent or represent an alkyl, an alkenyl, or an alkynyl, and R_{16} is absent or represents an amine, an imine, an amide, a phosphonate, a phosphine, a carbonyl, a carboxyl, a silyl, an oxygen, a sulfonyl, a sulfer, a selenium, or an ester;

each R_{19}, independently, is absent or represents one or more substituents of the heterocycle to which it is attached, each substituent independently selected from the group consisting of halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro, thiol amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, and $-(CH_2)_m-R_7$;

or any two or more of the R_{18} and R_{19} substituents are covalently linked to form a bridge substitution;

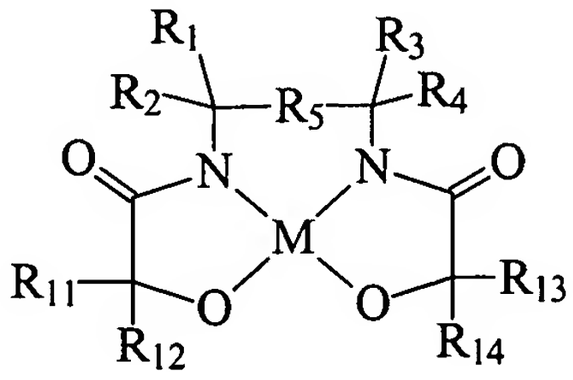
R_7 represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle;

m is zero or an integer in the range of 1 to 8;

M represents a transition metal; and

the catalyst is asymmetric;

the chiral catalyst represented by **112**,



112

in which

each of the substituents R_1, R_2, R_3, R_4, R_5, R_{11}, R_{12}, R_{13} and R_{14}, independently, represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro,

thiol amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or $-(CH_2)_m-R_7$;

or any two or more of the substituents taken together form a carbocycle or heterocycle having at least 4 atoms in the ring structure;

R_7 represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle;

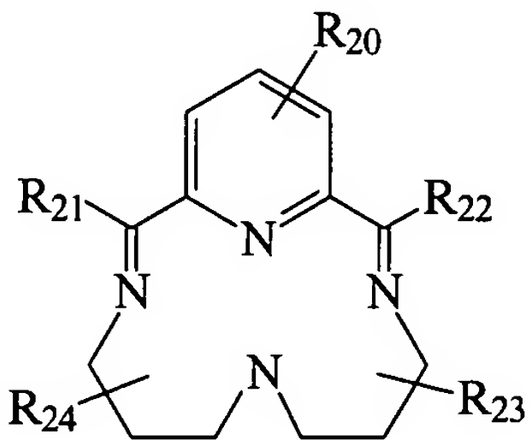
m is zero or an integer in the range of 1 to 8; and

M represents a transition metal;

if R_5 is absent, at least one of R_1 and R_2 is covalently bonded to at least one of R_3 and R_4; and

the catalyst is asymmetric;

the chiral catalyst represented by **114** and a complexed transition metal atom,



114

wherein

R_{21} and R_{22} each represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro, thiol amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or $-(CH_2)_m-R_7$;

R_{20} is absent or represents one or more substituents of the pyridine to which it is attached, each substituent independently selected from the group consisting of halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro, thiol amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or $-(CH_2)_m-R_7$;

R_{23} and R_{24} each independently are absent or represent one or more substituents of the 1,3-diiminopropyl to which they are attached, each substituent independently selected from the group consisting of halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro, thiol amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or $-(CH_2)_m-R_7$;

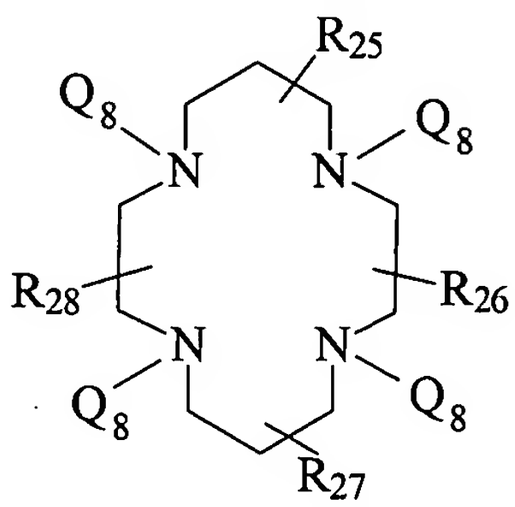
or any two or more of the R_{20}, R_{21}, R_{22}, R_{23} and R_{24} substituents are covalently linked to form a bridging substituent;

R_7 represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and

m is zero or an integer in the range of 1 to 8; and

the ligand is asymmetric; and

the chiral catalyst represented by **116** and a complexed transition metal atom,



116

in which

each of the substituents Q_8 indpendently, are absent or represent hydrogen or a lower alkyl;

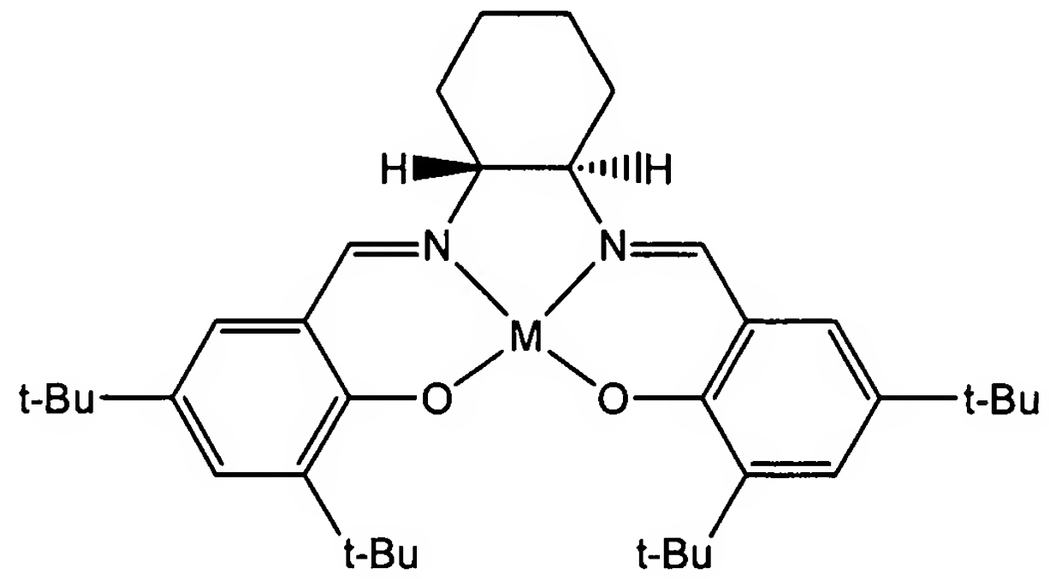
each of R_{25}, R_{26}, R_{27} and R_{28}, independently, represent one or more substituents on the ethyl or propyl diimine to which they are attached, which substituents are selected from the group of hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, alkoxyl, silyloxy, amino, nitro, thiol, amines, imines, amides, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, and $-(CH_2)_m-R_7$; or any two or more of the substituents taken together form a bridging substituent;

R_7 represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle, or a polycycle;

m is zero or an integer in the range of 1 to 8; and

the ligand is asymmetric.

101. **(previously presented)** The process of claim 94, wherein the non-racemic chiral catalyst is represented by structure **A** or its enantiomer:



A

wherein

M represents Co or $Co(O_2CR)$; and

R represents alkyl or aryl.

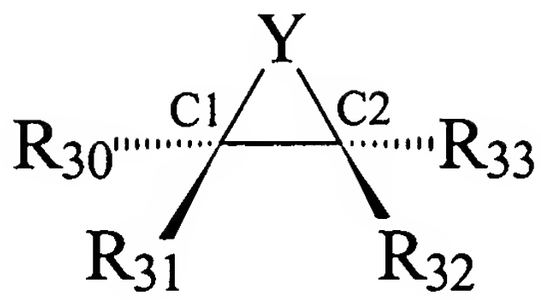
102. **(previously presented)** The process of claim 101, wherein said silyl azide is a trialkylsilyl azide.

103. **(previously presented)** The process of claim 101, wherein said silyl azide is trimethylsilyl azide.

104. **(previously presented)** The process of claim 94, wherein the tetradentate ligand has at least one Schiff base that complexes with the metal atom.

105. **(previously presented)** The process of claim 94, wherein the chiral catalyst has a molecular weight of less than 10,000 a.m.u.

106. **(currently amended)** The process of claim 94, wherein the chiral cyclic substrate is represented by the general formula **118**:



118

in which

Y represents O, S, N(R_{50}), C(R_{52})(R_{54}), or has the formula A-B-C; wherein R_{50} represents a hydrogen, an alkyl, a carbonyl-substituted alkyl, a carbonyl-substituted aryl, or a sulfonate, R_{52} and R_{54} each independently represent an electron-withdrawing group; A and C are independently absent, or represent a C_1-C_5 alkyl, O, S, carbonyl, or N(R_{50}); and B is a carbonyl, a thiocarbonyl, a phosphoryl, or a sulfonyl; and

R_{30}, R_{31}, R_{32}, and R_{33} represent organic or inorganic substituent which form a covalent bond with the C1 or C2 carbon atoms of **118**, and which permit formation of a stable ring structure including Y.

107. **(previously presented)** The process of claim 106, wherein the substituents R_{30}, R_{31}, R_{32}, and R_{33} each independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or -$(CH_2)_m$-R_7;

or any two or more of the substituents R_{30}, R_{31}, R_{32}, and R_{33} taken together form a carbocylic or heterocyclic ring having from 4 to 8 atoms in the ring structure; R_7 represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and

m is zero or an integer in the range of 1 to 8.

108. **(currently amended)** The process of claim 94, wherein the <u>chiral cyclic</u> cyclic substrate is selected from the group consisting of epoxides, aziridines, episulfides, cyclopropanes, cyclic carbonates, cyclic thiocarbonates, cyclic sulfates, cyclic anhydrides, cyclic phosphates, cyclic ureas, cyclic thioureas, lactams, thiolactams, lactones, thiolactones and sultones.

109. (**currently amended**) The process of claim 94, wherein the chiral cyclic cyclic substrate is an epoxide.

110. (**currently amended**) The process of claim 94, wherein the chiral cyclic cyclic substrate is a terminal epoxide.

111. (**previously presented**) The process of claim 94, wherein the non-racemic chiral catalyst is immobilized on an insoluble matrix.

112. (**previously presented**) The process of claim 94, wherein the cyclic substrate is immobilized on an insoluble matrix.

113. (**currently amended**) A kinetic resolution process, comprising the step of reacting a silyl azide and a mixture of stereoisomers of a chiral cyclic substrate in the presence of a non-racemic chiral catalyst to produce by kinetic resolution a stereoisomerically enriched cyclic substrate or a stereoisomerically enriched azide-substituted product or both, wherein said chiral cyclic substrate comprises a carbocycle or heterocycle having a reactive center susceptible to nucleophilic attack by said silyl azide, and said non-racemic chiral catalyst comprises an asymmetric tridentate ligand complexed with a metal atom, which complex has a trigonal planar or trigonal pyramidal geometry.

114. (**previously presented**) The process of claim 113, wherein said silyl azide is a trialkylsilyl azide.

115. (**previously presented**) The process of claim 113, wherein said silyl azide is trimethylsilyl azide.

116. (**previously presented**) The process of claim 113, wherein the metal atom is a transition metal from Groups 3-12 or from the lanthanide series.

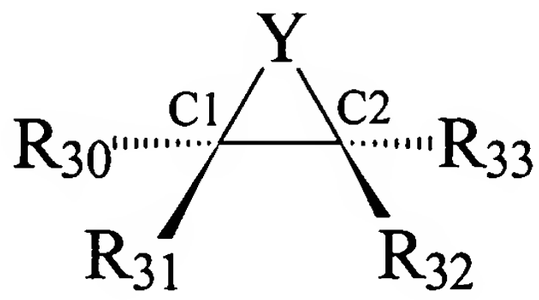
117. (**currently amended**) The process of claim 113, wherein the metal atom is selected from the group consisting of Co, Rh, and Ir.

118. (**previously presented**) The process of claim 113, wherein the metal atom is Co.

119. (**previously presented**) The process of claim 113, wherein the tridentate ligand has at least one Schiff base that complexes with the metal atom.

120. **(currently amended)** The process of claim 113, wherein the non-racemic chiral catalyst has a molecular weight of less than 10,000 a.m.u.

121. **(currently amended)** The process of claim 113, wherein the chiral cyclic substrate is represented by the general formula:



118

in which

Y represents O, S, $N(R_{50})$, $C(R_{52})(R_{54})$, or has the formula A-B-C; wherein R_{50} represents a hydrogen, an alkyl, a carbonyl-substituted alkyl, a carbonyl-substituted aryl, or a sulfonate, R_{52} and R_{54} each independently represent an electron-withdrawing group; A and C are independently absent, or represent a C_1-C_5 alkyl, O, S, carbonyl, or $N(R_{50})$; and B is a carbonyl, a thiocarbonyl, a phosphoryl, or a sulfonyl; and

R_{30}, R_{31}, R_{32}, and R_{33} represent organic or inorganic substituent which form a covalent bond with the C1 or C2 carbon atoms of **118**, and which permit formation of a stable ring structure including Y.

122. **(previously presented)** The process of claim 121, wherein the substituents R_{30}, R_{31}, R_{32}, and R_{33} each independently represent hydrogen, halogens, alkyls, alkenyls, alkynyls, hydroxyl, amino, nitro, thiol, amines, imines, amides, phosphoryls, phosphonates, phosphines, carbonyls, carboxyls, silyls, ethers, thioethers, sulfonyls, selenoethers, ketones, aldehydes, esters, or $-(CH_2)_m-R_7$;

or any two or more of the substituents R_{30}, R_{31}, R_{32}, and R_{33} taken together form a carbocyclic or heterocyclic ring having from 4 to 8 atoms in the ring structure;

R_7 represents an aryl, a cycloalkyl, a cycloalkenyl, a heterocycle or a polycycle; and

m is zero or an integer in the range of 1 to 8.

123. **(currently amended)** The process of claim 113, wherein the chiral cyclic substrate is selected from the group consisting of epoxides, aziridines, episulfides, cyclopropanes, cyclic carbonates, cyclic thiocarbonates, cyclic sulfates, cyclic anhydrides, cyclic phosphates, cyclic ureas, cyclic thioureas, lactams, thiolactams, lactones, thiolactones, and sultones.

124. **(currently amended)** The process of claim 113, wherein the chiral cyclic substrate is an epoxide.

125. **(currently amended)** The process of claim 113, wherein the chiral cyclic substrate is a terminal epoxide.

126. **(previously presented)** The process of claim 113, wherein the non-racemic chiral catalyst is immobilized on an insoluble matrix.

127. **(currently amended)** The process of claim 113, wherein the chiral cyclic substrate is immobilized on an insoluble matrix.

128. **(currently amended)** The process of any of claims 94-127, wherein said chiral cyclic substrate is racemic.